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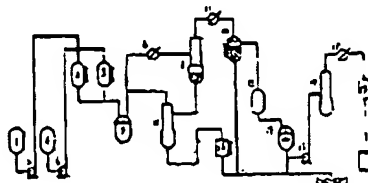
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[54]发明名称 一种生产氯代正丁烷的方法

[57]摘要

本发明涉及一种以正丁醇和盐酸为原料、不外加催化剂常压下连续生产氯代正丁烷的方法。由反应段、分离精制段、正丁醇回收段构成。物料经反应釜，进入恒沸蒸馏塔，在共沸点温度时，便有含少量水和正丁醇的氯代正丁烷以及微量盐酸蒸出，然后经水洗、精馏，获得精产品。恒沸蒸馏塔塔底混合物在塔釜中分两层，上层未反应的溶有少量水的正丁醇返回反应釜，下层溶有少量正丁醇的水以及少量盐酸进入共沸器，蒸出正丁醇和水也返回反应釜，继续反应。

本发明采用了恒沸蒸馏塔、共沸器和精馏塔，因而排出的污水量及其含酸量大大降低，得到的精产品含氯代正丁烷高于99.5%，正丁醇低于0.1%，二丁基醚低于0.01%。



权 利 要 求 书

1、一种以正丁醇和盐酸为原料、不外加催化剂、常压下连续生产氯代正丁烷的方法，其特征在于：

(1)合成反应后，使反应混合物进入恒沸蒸馏塔(9)，控制塔釜中混合物温度在70-80℃，塔顶温度在68±1℃时，蒸出共沸物含小量水和正丁醇的氯代正丁烷，塔底混合物在塔釜中分为两层，上层未反应的正丁醇和酸性水使之返回反应釜(7)，继续反应，下层大量水和正丁醇以及少量盐酸进入共沸器(10)，在共沸点时，其共沸物组成为大量正丁醇和少量水，由共沸器(10)蒸出，返回到反应釜(7)，继续反应；

(2)恒沸蒸馏塔(9)蒸出的共沸物经分离、水洗后，进入精馏塔(17)精馏。

2、按权利要求1所述的方法，其特征在于共沸器(10)塔釜混合物温度控制在102—108℃。

3、按权利要求1或2所述的方法，其特征在于收集沸程为77—79℃的精馏塔(17)的馏出物。

说明书

一种生产氯代正丁烷的方法

本发明涉及一种以正丁醇和盐酸为原料连续生产氯代正丁烷的方法，属有机合成工艺。这种氯代正丁烷特别适用于作为阴离子聚合催化剂用的正丁基锂的合成原料。

现有技术中，以正丁醇和盐酸或氯化氢为原料合成氯代正丁烷多在外加催化剂下制得，特别是以 $ZnCl_2$ 为催化剂的技术最多。该方法副反应多，反应中生成大量丁烯、二丁基醚及聚合树脂，产品中含有大量氯代仲丁烷，反应后 $ZnCl_2$ 的回收也很麻烦，不宜连续生产。

CZech148,798、CZech148,797 专利以 1 克分子正丁醇与 3 克分子过量的盐酸或氯化氢与溴化氢混合物回流反应制得氯代正丁烷。该方法使用的盐酸或与其与溴化氢的混合物用量过大，消耗多，对排出水中的醇和酸未提出处理措施。如果采用盐酸与溴化氢的混合物和正丁醇反应，则产物中将有溴代仲丁烷生成，这会降低氯代正丁烷的收率和纯度。

Ger (East) 138,470 专利是不外加催化剂下连续合成氯代正丁烷的方法。该方法以正丁醇和盐酸（浓度 30~34%）按重量比 1.32~1.38 比 1 连续地加入带有蒸馏塔、冷凝器和分离设备的耐酸容器内，在 98~102°C 的温度下反应，从塔顶连续地排出 50~54% 氯代正丁烷和 50~46% 水组成的混合物，并将这些水分离出来。生成的氯代正丁烷经过略带碱性的水洗涤，最后产品含 98.5~99.5%（重量）氯代正丁烷、0.5~1.5%（重量）正丁醇和 0.1%（重量）二丁基醚。该方法不足之处也是对排出水中的醇和酸未提出处理措施，且产品中含杂质量大，特别是二丁基醚的含量高。二丁基醚是一给电子试剂，在以正丁基锂为催化剂的阴离子聚合过程中混入该物质将会影响聚合反应，也影响正丁基锂贮存的稳定性，使之不易控制。作为合成阴离子聚合催化剂用的正丁基锂的原料，氯代正丁烷中含有二丁基醚是不希望的。

本发明旨在克服现有技术中的不足之处，提供一种排出污水量少、含醇和酸量低、产品纯度高、杂质（特别是二丁基醚）含量极低的，不外加

催化剂常压下连续生产的，特别适合于合成阴离子聚合催化剂正丁基锂的原料氯代正丁烷的工艺方法。

本发明的目的可以通过下述措施实现。

为了降低从反应混合物分离出来的水中的醇和酸的量，合成反应后，使反应混合物进入恒沸蒸馏塔。由于氯代正丁烷与水能生成共沸物，在共沸点温度时，会显著的提高共沸物组成中的氯代正丁烷含量，降低水含量。为此，在恒沸蒸馏塔塔顶温度控制在共沸点温度时，必将大大降低氯代正丁烷粗产品带出来的水量，而反应混合物中的大量水留在恒沸蒸馏塔的底部，其中也含有未反应的正丁醇和盐酸。该塔底混合物在塔釜中分为两层，上层由未反应的正丁醇和酸性水组成，下层由大量的水和正丁醇以及少量盐酸组成。上层液体使之返回反应釜，继续反应，这样便回收了一部分正丁醇和少排出了一部分含酸的水。

为了进一步回收未反应的正丁醇和减少污水排放量，并降低排出水的酸度，本发明还采用了共沸器装置，使恒沸蒸馏塔釜中的下层混合物进入该装置中。由于正丁醇与水也能生成共沸物，在共沸点温度时，其共沸物组成为大量正丁醇和少量水。由共沸器蒸出的上述共沸物也返回到反应釜，作为反应物料的一部分，继续反应。

如上所述，由反应釜出来的反应混合物中的酸性水经过两次分离后，均返回到反应釜中，剩下的由共沸器底部排出的酸性污水已大大减少，而且，在共沸出的正丁醇和水混合物返回反应釜时又起到了阻止、吸收反应釜中蒸出的盐酸的作用，因此，最后由共沸器排出的污水酸度也大大降低。与此同时，未反应的正丁醇又得到充分回收利用。

为了获得纯度高、杂质（特别是二丁基醚）含量极低的氯代正丁烷，对粗氯代正丁烷除了进行水洗外，本发明还采用了精馏手段。众所周知，少量正丁醇可溶于水，通过水洗除掉，而二丁基醚不溶于水，水洗法不能除去，故本发明采用了精馏工艺，使产品中二丁基醚含量降低到极低值。

根据上述措施，本发明的方法由反应段、分离精制段、正丁醇回收段三个工艺程序组成。在反应段，按摩尔比1~1.1比1的盐酸和正丁醇连续地

加入反应釜中，生成氯代正丁烷、水和部分未反应的正丁醇一起被蒸出，并夹带少量盐酸，连续进入分离精制段的恒沸蒸馏塔，在共沸点温度时，便有含少量水、正丁醇和微量盐酸的氯代正丁烷蒸出，再经分层处理，得氯代正丁烷粗产品，然后水洗、精馏，获得精产品。恒沸蒸馏塔塔底混合物在塔釜中分为两层：上层未反应的正丁醇和酸性水返回反应釜；下层大量的水和正丁醇以及少量盐酸进入正丁醇回收段的共沸器，蒸出正丁醇和水也返回反应釜，继续反应。

采用本发明所述的方法，使得工艺过程排出的污水及其含酸量大大降低，得到的精产品含氯代正丁烷高于99.5%（重量）、正丁醇低于0.1%（重量）、二丁基醚低于0.01%（重量）。

下面结合实施例对本发明作进一步陈述。

附图为本发明实施例的工艺流程图。

本实施例的反应段由正丁醇贮罐(1)、盐酸贮罐(4)、泵(3)、(6)、正丁醇计量罐(2)、盐酸计量罐(5)、反应釜(7)组成。反应釜(7)的容积为1米³。

将正丁醇贮罐(1)中的正丁醇经泵(3)送至正丁醇计量罐(2)。经计量后，将445公斤正丁醇送至反应釜(7)中。然后，将盐酸贮罐(4)中浓度为30—31%的工业盐酸经泵(6)送至盐酸计量罐(5)中，经计量后，将250公斤工业盐酸也加入反应釜(7)中。

打开反应釜(7)蒸汽夹套的进出口阀，通蒸汽加热，使釜中温度达98~105℃，物料在沸腾下反应，生成的氯代正丁烷、水、部分未反应的正丁醇和少量盐酸一起被蒸出。与此同时，开始按每小时加13~17公升正丁醇和24—32公升工业盐酸的速度连续地往反应釜(7)中补加物料。

分离精制段由冷凝器(8)、(11)、(18)、恒沸蒸馏塔(9)、氯代正丁烷分层罐(12)、粗氯代正丁烷贮罐(13)、水洗釜(15)、泵(16)、精馏塔(17)、精氯代正丁烷贮罐(19)组成。恒沸蒸馏塔(9)由一个理论板数大于14的塔身和塔釜组成，精馏塔(17)由理论板数大于10的塔身和塔釜组成。均使用耐酸材料。

从反应釜中(7)中蒸出的氯代正丁烷、水、部分未反应的正丁醇和少量

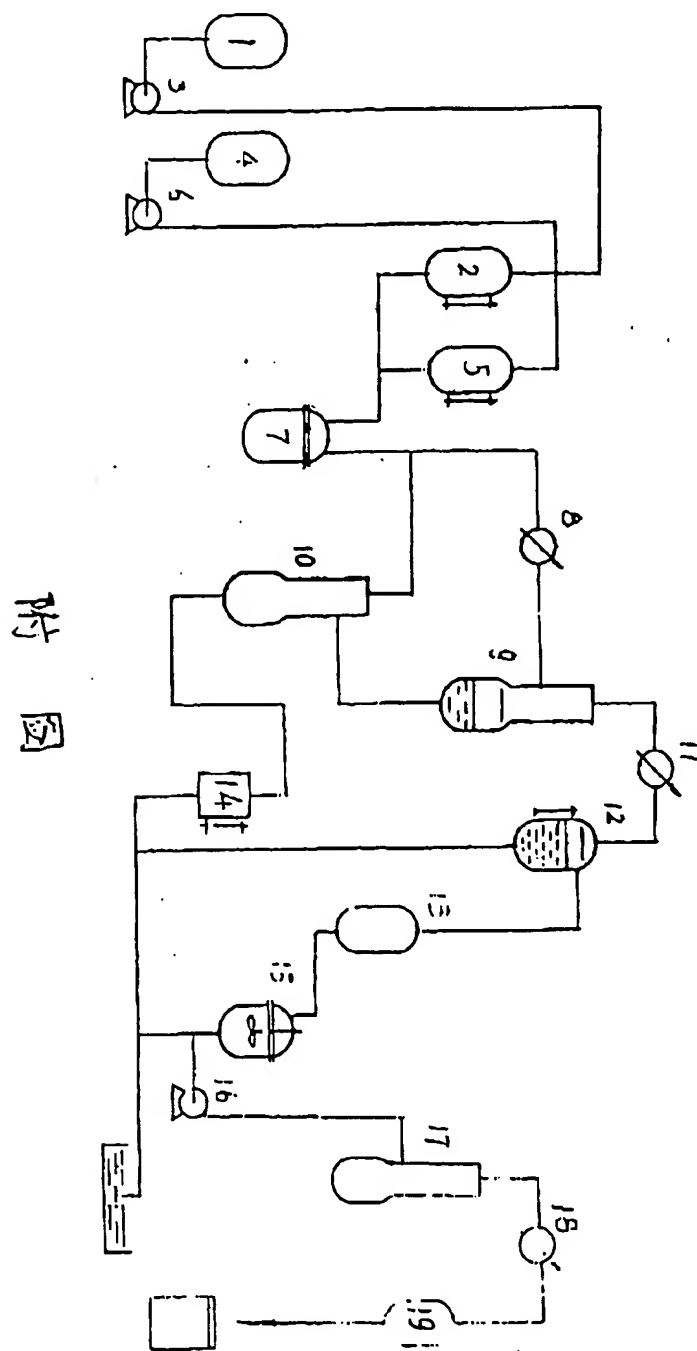
盐酸经冷凝器(8)进入恒沸蒸馏塔(9)中,调整冷凝器(11)的冷却水量和恒沸蒸馏塔(9)釜夹层中的蒸汽流量,将塔釜中混合物温度控制在70-80°C,在恒沸蒸馏塔(9)塔顶便有含小量水和正丁醇的氯代正丁烷以及微量盐酸蒸出。控制塔顶全凝器的冷却水流量,使塔顶温度保持在68±1°C,则蒸出的共沸物中氯代正丁烷含量可提高到93.4% (重量)、水含量6.6% (重量)。蒸出的共沸物经冷凝器(11)冷却后进入氯代正丁烷分层罐(12)。在该分层罐(12)中,经分层,氯代正丁烷和水分成两相,下层水由底部排至中和池,上层得到纯度为98.22% (重量) 的氯代正丁烷溢流至粗氯代正丁烷贮罐(13)中,经水洗釜(15),用同体积的工业水洗涤三次,使正丁醇含量低于0.1% (重量),然后通过泵(16)送至精馏塔(17)中进行精馏,收集沸程为77-79°C的馏出物,使二丁基醚含量低于0.01% (重量)。再经冷凝器(18)装入精氯代正丁烷贮罐(19)。在上述工艺条件下,最后获得的精产品经色谱分析,含氯代正丁烷99.76% (重量)、正丁醇0.033% (重量)、二丁基醚0.002% (重量)、氯代仲丁烷0.136% (重量)、丁烯0.063% (重量)。

正丁醇回收段由共沸器(10)、排水计量罐(14)组成。共沸器(10)是由蒸馏塔釜和塔身组成,用耐酸材料制成,其共沸物出口直接与反应釜(7)相连。

在恒沸蒸馏塔(9)釜中的混合物分为两相,当釜中的混合物达到一定高度时,上层含水20% (重量)的正丁醇溢流返回反应釜(7),下层约含7% (重量)正丁醇的酸性水溶液进入共沸器(10)。打开共沸器(10)夹套的蒸汽进出口阀,通蒸汽加热,使液体升温至102-108°C时,蒸出约含62% (重量)正丁醇的共沸物也返回反应釜(7),从而共沸器(10)底部排出污水中氯化氢含量低于1% (重量)、正丁醇含量低于0.1% (重量)。该污水通过排水计量罐(14)流入中和池。

本实施例的装置每小时生产14.42公斤高纯度的氯代正丁烷。收率为理论值的90%。

说明书附图



附图

CPCH0163787 对比文件译文

Claims

What is claimed is:

1. A process for the continuous production of a chlorinated n-butane at an ordinary pressure using n-butanol and hydrochloric acid as raw materials without the addition of a catalyst, characterized in .

(1) supplying the reaction mixtures into the constant-boiling column (9) after the synthesis reaction, controlling the temperature of the mixtures in the column kettle at 70-80°C, and the temperature of the top part of the column at 68 ± 1 °C, distilling off azeotrope--chlorinated n-butane containing a small amount of water and n-butanol; dividing the mixtures at the bottom of the column into two layers, wherein the unreacted n-butanol and acidic water in the upper layer are returned back to the reaction kettle (7) for the further reaction, and a large amount of water and n-butanol and a small amount of hydrochloric acid in the lower layer are sent to the co-boiling device (10); said azeotrope comprising a large amount of n-butanol and a small amount of water at the co-boiling point, which are distilled off from the co-boiling device (10) and sent back to the reaction kettle (7) for the further reaction;

(2) after being separated and water-washed, the azeotrope distilled from the constant-boiling column (9) flowing into the rectification column (17) for the rectification .

2. A process according to claim 1, characterized in controlling the temperature of the mixtures in the column kettle of the co-boiling device (10) at 102-108°C.

3. A process according to claim 1 or 2, characterized in collecting the distillates having a boiling range of from 77-79°C from the rectification column (17).

A process for the production of chlorinated n-butane

The present invention relates to a process for the continuous production of a chlorinated n-butane using n-butanol and hydrochloric acid as raw materials, which is an organic synthesis technique. Such chlorinated n-butanenes are especially suitable for synthesizing n-butyl lithium as an anionic polymerization catalyst.

In the prior art, the synthesis of chlorinated n-butanenes using n-butanol and hydrochloric acid or hydrogen chloride as raw materials is typically carried out with the addition of the catalysts, particularly the technique of using ZnCl_2 as the catalyst under most circumstances. However, there are many side reactions in the process, and a large amount of butylenes, dibutyl ethers and polymeric resins are produced during the reaction. In addition, the products comprise a plurality of chlorinated sec-butanenes, and it is difficult to recover ZnCl_2 after the reaction. Thus, the process is not suitable for the continuous production.

It is disclosed in the patent documents numbered CZech148,798 and CZech148,797 that 1 gram molecule n-butanol reflux-reacts with 3 gram molecule excessive hydrochloric acid or a mixture of hydrogen chloride and hydrogen bromide to produce chlorinated n-butanenes. The reaction consumes much hydrochloric acid and the mixture of hydrogen chloride and hydrogen bromide, and there are not any treatment measures for alcohols and acids in the water discharged thereof. If the mixture of hydrochloric acid and hydrogen bromide reacts with n-butanol, bromo-sec-butane will be produced in the products, which will decrease the yield and purity of chlorinated n-butanenes.

The patent document Ger (East) 138,470 relates to a process for the continuous synthesis of chlorinated n-butanenes without the addition of the catalysts, comprising continuously adding n-butanol and hydrochloric acid (having a concentration of 30-34%) in a weight ratio of 1.32-1.38 to 1 into an acid-resistant container comprising a distillation column, a condenser and a separating device, reacting at a temperature of from 98 to 102°C, continuously discharging the mixtures comprising 50-54% of chlorinated n-butanenes and 50-46% of water from the top of the column,

and then separating water therefrom. After chlorinated n-butanes formed are washed with the slightly alkaline water, the final products comprise 98.5-99.5% by weight of chlorinated n-butane, 0.5-1.5% by weight of n-butanols and 0.1% by weight of dibutyl ethers. The deficiencies of said process also lie in that there are not any treatment measures for alcohols and acids in the water discharged thereof. Moreover, the products comprise a large amount of impurities, in particular a high content of dibutyl ethers. Dibutyl ether which is an electron donating agent will have an effect on the polymerization reaction during the anionic polymerization process using n-butyl lithium as the catalyst, and also the storage stability of n-butyl lithium so as to be difficult to be controlled. It is undesirable that chlorinated n-butanes as raw materials for synthesizing n-butyl lithium as an anionic polymerization catalyst comprise dibutyl ethers.

The present invention aims to overcome the deficiencies in the prior art, and provide a technological process for the continuous production of chlorinated n-butanes as raw materials, especially suitable for synthesizing n-butyl lithium as an anionic polymerization catalyst, at an ordinary pressure without the addition of a catalyst, having a small amount of the sewage discharged thereof, a low content of alcohols and acids, a high purity of the product, and a greatly low content of the impurities (especially, dibutyl ether).

The object of the present invention can be achieved via the following measures.

In order to reduce the content of alcohols and acids in the water separated from the reaction mixtures, the reaction mixtures are fed into the constant-boiling distillation column after the synthesis reaction. Since chlorinated n-butanes and water may form an azeotrope, the content of chlorinated n-butanes in an azeotrope will be notably increased at an azeotropic temperature so as to decrease the content of water. Thus, when the temperature at the top of the constant-boiling distillation column is controlled at an azeotropic temperature, water taken out by the crude products of chlorinated n-butanes will be greatly reduced. Moreover, much of the water in the reaction mixtures remains at the bottom of the constant-boiling distillation column, wherein the unreacted n-butanol and

hydrochloric acid are comprised therein. The mixtures at the bottom of the column are divided into two layers in the column kettle, wherein the upper layer comprises the unreacted n-butanol and acidic water, and the lower layer comprises a large amount of water and n-butanol and a small amount of hydrochloric acid. The liquid in the upper layer is sent back to the reaction kettle for the further reaction, so as to recover part of n-butanol and reduce the amount of the acidic water discharged thereof.

In order to further recover the unreacted n-butanol and reduce the amount of the sewage discharged thereof, and decrease the acidity of the sewage, the co-boiling device is also used in the present invention, and the mixtures in the lower layer of the constant-boiling distillation column are sent into said device. Since n-butanol and water can also form an azeotrope, the azeotrope comprises a large amount of n-butanol and a small amount of water at an azeotropic temperature. Moreover, said azeotrope distilled from the co-boiling device is also sent back to the reaction kettle, and further participates in the reaction as part of the reaction materials.

As stated above, acidic water in the reaction mixtures from the reaction kettle is sent back to the reaction kettle after two separations, and the acidic sewage discharged from the bottom of the co-boiling device has been greatly reduced, and functions as preventing and absorbing hydrochloric acid distilled from the reaction kettle when the co-boiled mixtures of n-butanol and water are sent back to the reaction kettle. Thus, the acidity of the sewage discharged from the co-boiling device has also been greatly reduced. Meanwhile, the unreacted n-butanol is sufficiently recovered.

Besides water washing the crude chlorinated n-butanes, the rectification method is also used in the present invention for obtaining chlorinated n-butane having a high purity and a greatly low content of impurities (especially, dibutyl ether). It is well known that a small amount of n-butanol is soluble in water, and can be removed by water washing, whereas dibutyl ether is insoluble in water, and cannot be removed by water washing. Thus, the rectification process is used in the present invention so as to decrease the content of dibutyl ether in the products to an extremely low extent.

According to the aforesaid measures, the process of the present invention comprises three technological procedures consisting of reaction stage, separating and refining stage, and n-butanol recovery stage. During the reaction stage, hydrochloric acid and n-butanol in a molar ratio of 1-1.1:1 are continuously added into the reaction kettle. Chlorinated n-butanes formed, water and part of the unreacted n-butanol together are distilled off with a small amount of hydrochloric acid, and then continuously added into the constant-boiling distillation column during the separating and refining stage. Then, chlorinated n-butanes containing a small amount of water, n-butanol and little hydrochloric acid are distilled off at an azeotropic temperature, and stratified to obtain the crude products of chlorinated n-butanes. The refined products are obtained after water washing and rectifying the crude products. The mixtures at the bottom of the constant-boiling distillation column are divided into two layers in the column kettle, wherein the unreacted n-butanol and acidic water in the upper layer are sent back to the reaction kettle; a large amount of water and n-butanol and a small amount of hydrochloric acid in the lower layer are added into the co-boiling device during the n-butanol recovery stage, and n-butanol and water distilled off are also sent back to the reaction kettle for the further reaction.

The sewage discharged during the technological procedure and the acid content thereof are greatly decreased by using the process as stated in the present invention, and chlorinated n-butane in the refined products is 99.5% by weight, n-butanol is less than 0.1% by weight, and dibutyl ether is less than 0.01% by weight.

The present invention is further explained as follows by combining with the example.

The drawings are the process flow diagram of the example of the present invention.

The reaction stage in the example comprises the n-butanol stock tank (1), the hydrochloric acid stock tank (4), the pumps (3) and (6), the n-butanol measuring tank (2), the hydrochloric acid measuring tank (5) and the reaction kettle (7), wherein the kettle has a volume of 1 m³.

The n-butanol in the n-butanol stock tank (1) is sent to the n-butanol measuring tank (2) via the pump (3). After the measurement, 445 kg n-butanol is sent to the reaction kettle (7). Then, commercial hydrochloric acid having a concentration of 30-31% in the hydrochloric acid measuring tank (4) is sent to the hydrochloric acid measuring tank (5). After the measurement, 250 kg commercial hydrochloric acid is also sent to the reaction kettle (7).

The inlet and outlet valves of the steam jacket on the reaction kettle (7) are opened so as to pass over the steam and heat up the kettle to a temperature of from 98 to 105°C in the kettle. The materials react with each other under the boiling conditions, and chlorinated n-butane formed thereof, water, part of the unreacted n-butanol and a small amount of hydrochloric acid together are distilled off. Meanwhile, the materials are supplied into the reaction kettle (7) at a rate of 13-17 kg n-butanol and 24-32 kg commercial hydrochloric acid per hour.

The separating and refining stage comprises the condensers (8), (11) and (18), the constant-boiling distillation column (9), the stratifying tank (12), the crude chlorinated n-butane stock tank (13), the water-washing kettle (15), the pump (16), the rectification column (17) and the refined n-butane stock tank (19). The constant-boiling distillation column (9) comprises a column body having column plates higher than 10 in theory, and a column kettle; and the rectification column (17) comprises a column body having column plates higher than 10 in theory, and a column kettle. Moreover, both are made of acid-resistant materials.

Chlorinated n-butane distilled off from the reaction kettle (7), water, part of the unreacted n-butanol and a small amount of hydrochloric acid are sent to the constant-boiling distillation column (9) via the condenser (8), and the temperature of the mixture in the column kettle is controlled at 70-80°C by adjusting the amount of the cooling water in the condenser (11), and the flow rate of the stream in the kettle interface-layer of the constant-boiling distillation column (9). Then, chlorinated n-butane containing a small amount of water and n-butanol, and little hydrochloric acid are distilled off at the top of the constant-boiling distillation column (9). The temperature at the top of the column is controlled at $68 \pm 1^\circ\text{C}$ by adjusting the flow rate of the cooling water in the total condenser at the

top of the column; and the content of chlorinated n-butane in the azeotrope distilled off may be increased to 93.4% by weight, and water is 6.6% by weight. The azeotrope distilled off comes into the chlorinated n-butane stratifying tank (12) after cooled in the condenser (11). In the stratifying tank (12), chlorinated n-butane and water are divided into two phases after the stratification, wherein water in the lower layer is discharged from the bottom into the neutralization tank, and chlorinated n-butane having a purity of 98.22% by weight in the upper layer overflows into the crude chlorinated n-butane stock tank (13). Then, said chlorinated n-butaness are washed three times in the water-washing kettle with industrial water having the same volume, so as to make the content of n-butanol lower than 0.1% by weight, and sent to the rectification column (17) via the pump (16) for the rectification. The distillates having a boiling range of from 77-79°C are collected, so as to make the content of dibutyl ether lower than 0.01% by weight. Afterwards, said distillates are loaded into the refined n-butane stock tank (19) via the condenser (18). Under the aforesaid technological conditions and upon the chromatographic analysis, the refined products obtained ultimately comprises 99.76% by weight of chlorinated n-butane, 0.033% by weight of n-butanol, 0.002% by weight of dibutyl ether, 0.136% by weight of chlorinated sec-butane and 0.063% by weight of butylene.

The n-butanol recovery stage comprises the co-boiling device (10) and the water-discharging measuring tank (14), wherein the co-boiling device comprises the distillation column kettle and body made of acid-resistant materials, and the outlet of the azeotrope directly links with the reaction kettle (7).

The mixtures in the kettle of the constant-boiling distillation column (9) are divided into two phases. When the mixtures in the kettle reach some height, n-butanol containing 20% by weight of water in the upper layer overflows back to the reaction kettle (7), and acidic aqueous solution containing 7% by weight of n-butanol enters the co-boiling device (10). The inlet and outlet valves of the steam jacket on the co-boiling device (10) are opened so as to pass over the stream and heat up the liquid to a temperature of from 102 to 108°C. The distilled azeotrope containing 62% by weight of n-butanol are returned back to the reaction kettle (7), so that the content of hydrogen chloride in the sewage discharged from the

bottom of the co-boiling device (10) is lower than 1% by weight, and the content of n-butanol is lower than 0.1% by weight. The sewage flows into the neutralization tank via the water-discharging measuring tank (14).

The device of the present example can produce 14.42 kg of chlorinated n-butane having a high purity per hour, and the yield thereof is 90% of the theoretical value.